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## Characterization of type III kerogen from Tyrolean shale (Hahntennjoch, Austria) based on its oxidation products

S. BAJC<sup>1\*</sup>, O. CVETKOVIĆ<sup>1#</sup>, A. AMBLÈS<sup>2</sup> and D. VITOROVIĆ<sup>1#</sup>

<sup>1</sup>Center of Chemistry, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia and <sup>2</sup>Department of Chemistry, Faculty of Science, University of Poitiers, 40, Av. du Recteur Pineau, 86022 Poitiers, France

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**Abstract:** A 29-step alkaline permanganate degradation of type III kerogen from Tyrolean (Hahntennjoch, Austria) oil shale was performed. A high yield of oxidation products was obtained (93.7 % relative to the original kerogen): 0.5 % neutrals and bases, 19.5 % ether-soluble acids and 58.9 % of precipitated (PA). A substantial amount of kerogen carbon (14.8 %) was oxidized into carbon dioxide. The organic residue remaining after the final oxidation step was 6.9 %. The PA components were further oxidized and the total yields relative to original PA were 1.0 % neutrals and bases and 59.0 % ether-soluble acids, the non-degraded residue being 29.3 %. Detailed quantitative and qualitative analysis of all oxidation products suggested the Tyrolean shale kerogen to be a heterogeneous macromolecular substance consisting of three types of structures differing in composition and susceptibility towards alkaline permanganate: the first, resistant, presumably composed of aromatic structures linked by resorcinol etheral bonds; the second, combined in nature, the aliphatic part comprising methyl-substituents and short cross-links, both easily oxidized into CO<sub>2</sub>, water and low molecular weight acids and aromatic structures yielding aromatic di- and tri-carboxylic acids as oxidation products; finally the third, composed of aliphatic cross-links and substituents, alicyclic (and/or heterocyclic) and some aromatic structures, bound into units moderately resistant towards oxidation. The overall yields of kerogen and PA oxidation products lead towards a balance between aromatic, alkane mono- and dicarboxylic and alkanepolycarboxylic acids, suggesting a shift of the structure of Tyrolean shale kerogen from typical aromatic reference type III towards a heterogeneous aromatic-aliphatic-alicyclic type structure.

**Keywords:** Tyrolean shale; type III kerogen; structural characterization; alkaline permanganate degradation; oxidation products.

\*Corresponding author. E-mail: sbajc@chem.bg.ac.yu

# Serbian Chemical society member.

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## INTRODUCTION

Structural elucidation of kerogen, the most abundant form of organic matter in the crust of the Earth, is of continuing organic geochemical interest.<sup>1</sup> A graph of atomic H/C vs. O/C ratios, named van Krevelen diagram, for long served for the classification of kerogens into three principal reference types (I, II and III) based on their similar structural evolution paths.<sup>2</sup> Yet, it was shown that controlled oxidative degradation offered a more precise structural differentiation and structural interpretation of the kerogens. Namely, very high yields of identifiable kerogen oxidation products with retained precursor structural characteristics, obtained by an optimized multi-step oxidative degradation method, clearly demonstrated remarkable differences between kerogens which, according to their atomic H/C and O/C ratios, appeared to be similar.<sup>3-7</sup> Thus, the position in the van Krevelen diagram, determined by the overall nature of the elemental analysis, was shown to be insufficient to fully characterize a kerogen.

Consequently, the proportions of various kinds of acidic oxidation products observed in several oxidation studies were used as a basis for an advantageous characterization and classification of kerogens, materialized in the form of an aliphatic/aromatic/alkane-polycarboxylic + cycloalkanoic acids triangular diagram, these types of acids being the main oxidation products of kerogen aliphatic, aromatic and alicyclic/heterocyclic structures, respectively.

Parallel studies of twelve samples of type I (4), type II (4), intermediate type I-II (3), and type III (1) kerogens from shales of various geographic origin, using a similar or identical standard optimized alkaline permanganate method, have so far been carried out. These oxidative degradation studies neglected type III kerogens. Namely, as shown, only one sample of type III kerogen, *i.e.*, kerogen originating from the Mannville shale, Canada,<sup>8</sup> was examined until now, and that was even before the method was completely optimized. In order to supplement data on structural characteristics of type III kerogens and thus provide a basis for comparison of their structures, a type III kerogen from a Tyrolean (Austria) "Hauptdolomit" Triassic sediment was studied using the optimized alkaline permanganate degradation method and the results reported in this paper.

## EXPERIMENTAL

*Sample preparation*

The investigated oil shale sample (No. H124C) originated from a Tyrolean (Austria) "Hauptdolomit" Triassic sediment. It was taken at 48.4 m from an outcrop located by the road to Hahntennjoch, *ca.* 3 km west of Imst. The vitrinite reflectance of this sample was found to be 1.38 % Ro.

The powdered sample contained 0.2 % moisture, 1.0 % bitumen, and 3.7 % kerogen. The kerogen concentrate was prepared by the method described by Vitorović *et al.*<sup>9</sup> Most of the sample (85.8 %) was soluble in dilute (1:4) hydrochloric acid. The resulting HCl concentrate was treated with a mixture of hydrochloric and hydrofluoric acids. The yield of HCl/HF concentrate was 4.3 % relative to original, dry sample. Its bitumen was eliminated by extraction

with a mixture of benzene and methanol. The final HCl/HF kerogen concentrate contained 84.6 % kerogen, composed of 80.78 % C, 5.11 % H, 0.80 % N and 13.31 % O + S<sub>org</sub> (by difference). The atomic H/C and O/C ratios, calculated on the basis of the elemental analysis, were 0.76 and 0.125, respectively, corresponding to the reference type III kerogen.<sup>10</sup>

#### Oxidative degradation

The HCl/HF kerogen concentrate (2.95 g, containing 2.5 g kerogen) was oxidized in 29 steps at 75 °C with 0.5 g KMnO<sub>4</sub> in 10 cm<sup>3</sup> water and 100 cm<sup>3</sup> 1.0 % KOH per step, according to standard degradation scheme described by Vitorović *et al.*<sup>3</sup> The same ratio of oxidant vs. substrate was used in all previous kerogen structural studies by the authors. The end of reaction in each step was established by the disappearance of the violet and green colors. The alkaline solution containing the oxidation products was removed by centrifugation and thorough washing of the remaining solids.

Following every five steps, the accumulated MnO<sub>2</sub> was removed by treatment with an excess of 5.0 % oxalic acid solution (50 cm<sup>3</sup> plus 10 cm<sup>3</sup> 2M H<sub>2</sub>SO<sub>4</sub>) and thorough rinsing with distilled water. The final oxidation mixture was treated in a similar way. The solid residue was dried at 80 °C and analyzed for organic matter.

The reduction periods gradually increased during the oxidation procedure as shown in Fig. 1. The occasional shorter reduction periods (6<sup>th</sup>, 11<sup>th</sup>, 16<sup>th</sup>, and 21<sup>st</sup> steps) followed the removal of MnO<sub>2</sub>. Hence, the shorter reduction periods were probably a result of the increased reactivity of the "purified" kerogen concentrate.

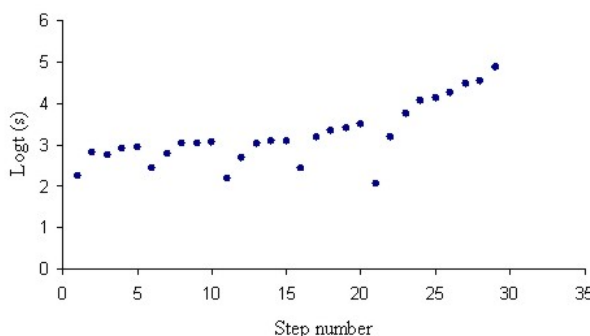


Fig. 1. Duration of successive degradation steps.

The last, 29<sup>th</sup> portion of permanganate was not fully reduced after 23 h. The 29<sup>th</sup> step was, therefore, taken as the final degradation step.

The products from each five steps, as well as the products of the last four steps, were combined (6 fractions in total) and worked up separately according to the procedure described by Amblès *et al.*<sup>11</sup> A 100 cm<sup>3</sup> aliquot was separated from each fraction, aimed at determining the amount of carbon dioxide produced by oxidation of the kerogen. A modified Partridge and Schroeder method was used for this purpose.<sup>12,13</sup>

Three types of products were isolated from the six fractions: neutrals and bases, ether-soluble acids and precipitated acids. The remaining aqueous solutions were made alkaline, evaporated to a small volume, acidified with HCl and finally diluted to standard 100 cm<sup>3</sup>. The soluble acids were then extracted with ether.<sup>14</sup> Consequently, five types of products were obtained from each fraction: neutrals and bases (not examined), ether-soluble acids [marked Ty 1(1) to Ty 6(1)], precipitated (ether-insoluble) acids, acids from aqueous solutions [Ty 1(2) to Ty 6(2)], and kerogen carbon oxidized to carbon dioxide.

#### *Further degradation of precipitated acids*

The precipitated acids from all six fractions were combined (1.48 g) and homogenized by redissolving in 1.0 % KOH and co-precipitation with 1:1 HCl. An aliquot of 0.88 g was further oxidized in 8 steps with small amounts of  $\text{KMnO}_4$  (0.45 g per step in 8 cm<sup>3</sup> water and 88 cm<sup>3</sup> 1.0 % KOH). Prior to the addition of each new portion of permanganate, the acids were dissolved in KOH solution and heated to the standard reaction temperature of 75 °C. After the reduction of each portion of reagent, the reaction mixture was treated in the same way as the kerogen degradation products. The thus obtained precipitated acids were each time further oxidized in the next step with a new portion of permanganate. The produced  $\text{MnO}_2$  was reduced after the fifth step. The products from the 1<sup>st</sup>–5<sup>th</sup> and 6<sup>th</sup>–8<sup>th</sup> step were combined into two fractions. The portion of permanganate in the last, the 8<sup>th</sup>, step was not fully reduced after more than 30 h. The precipitated acids obtained in the 8<sup>th</sup> step were washed with distilled water and dried at 100 °C. For further investigation, the ether-soluble acids were combined into two fractions [marked Ty P1 (1) and Ty P2 (1)]. Acids from the corresponding aqueous solutions were also isolated [marked Ty P1 (2) and Ty P2 (2)].

#### *Investigation of soluble acids*

All the soluble acids were methylated with ethereal diazomethane. The esters were analyzed by GC and identified by GC–MS. The GC separations were carried out in a Packard Model 427 gas chromatograph, using a 25 m fused silica WCOT CP Sil 5 (0.16  $\mu\text{m}$ ) capillary column, coupled to an integrator-calculator Spectra Physics System 1. The temperature of the column was programmed from 70 °C (10 min isothermally) to 300 °C, at 2 °C min<sup>-1</sup>. Nitrogen was used as the carrier gas.

The GC–MS analyses were performed with a system consisting of a gas chromatograph Perkin-Elmer Sigma 3 coupled to a mass spectrometer Kratos MS 25. The column temperature was also programmed from 70 to 300 °C at 2 °C min<sup>-1</sup>. The mass spectra were recorded for all the significant separated peaks.

Identification of the individual components was accomplished by comparison with the mass spectra of available authentic compounds, literature data and the available spectral data bank.

Efficient capillary GC separations, combined with the integrator-calculator service, enabled the quantitative evaluation of the proportions of the various kinds of ether-soluble acids obtained from: (a) oxidation of the kerogen concentrate, (b) oxidation of the precipitated acids and (c) aqueous solutions produced in both of these oxidations.

### RESULTS

#### *Oxidative degradation of kerogen concentrate*

Twenty-nine steps were necessary for the degradation of the kerogen and a total amount of 14.5 g  $\text{KMnO}_4$  was consumed (5.8 g  $\text{KMnO}_4$  per g of kerogen). Approximately 66 h were required for the 29 steps. As already indicated, in the 29<sup>th</sup> step, which lasted 23 h, the  $\text{KMnO}_4$  had not been fully reduced.

The yields of products in the six oxidation stages are shown in Fig. 2. The yields of neutrals and bases, total ether-soluble acids (0.27 g of ether soluble acids and 0.21 g of acids isolated from aqueous solutions), and precipitated acids (1.48 g) were 0.5, 19.5 and 58.9 %, respectively, relative to the original kerogen, the total yield being 78.9 %. Hence, the participation of neutrals and bases, total ether-soluble acids, and precipitated acids, in the total degradation product was

0.69, 26.76 and 74.64 %, respectively. The ratio of insoluble vs. soluble acids was 3.02.

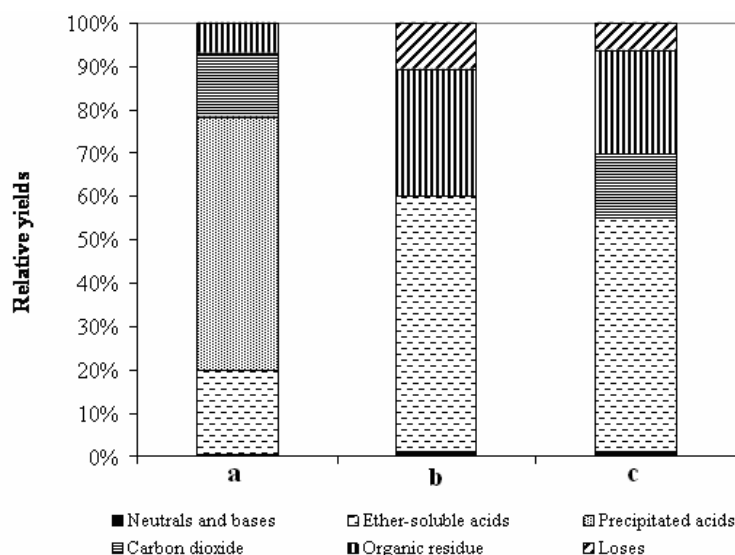


Fig. 2. Yield of products obtained by oxidative degradation of kerogen concentrate (a), precipitated acids (b) and total yield obtained by oxidative degradation of kerogen concentrate and precipitated acids (c).

Analysis of the aliquots of the six fractions of the aqueous solutions containing soluble kerogen oxidation products by a modified Partridge–Schroeder method<sup>13</sup> showed a substantial amount of kerogen carbon, 0.37 g, had been oxidized into carbon dioxide (14.8 % relative to the original kerogen).

The solid residue in the final step (0.20 g) contained 0.17 g organic matter (6.9 % relative to the original kerogen).

#### *Ether-soluble acids*

One of the gas chromatograms of the ether-soluble acids in the form of their methyl esters is given as an example in Fig. 3.

The GC–MS analysis of the various fractions revealed the presence of different aromatic mono-, di-, tri- and tetra-carboxylic acids, minor amounts of saturated normal monocarboxylic and  $\alpha,\omega$ -dicarboxylic acids, as well as aromatic acids, anhydrides and several unidentified compounds. Similar types of products were isolated from the corresponding aqueous solutions, *i.e.*, different aromatic mono-, di-, tri- and tetracarboxylic acids as major constituents, with minor amounts of aliphatic mono- and dicarboxylic acids, aromatic acids, anhydrides, saturated hydrocarbons and several unidentified compounds. All the identified ether-soluble oxidation products are listed in Table I.

### Further oxidation of the precipitated acids

Eight steps were carried out in the degradation of an aliquot of 0.88 g of precipitated acids. A total amount of 3.6 g of  $\text{KMnO}_4$  was consumed (4.1 g per g of acids).

The yields of products obtained in the degradation of precipitated acids are shown in Fig. 2. The total yields of neutrals and bases and ether-soluble acids (including the acids isolated from aqueous solutions) *i.e.*, 0.48 of ether-soluble acids and 0.04 g of acids from aqueous solutions were 1.0 % and 59.0 %, respectively, relative to original precipitated acids. A gas chromatogram of one of the fractions of these ether-soluble acids is shown as an example in Fig. 4. The yield of precipitated acids in the eight steps (non-degraded precipitated acids) was 0.26 g (29.3 %).

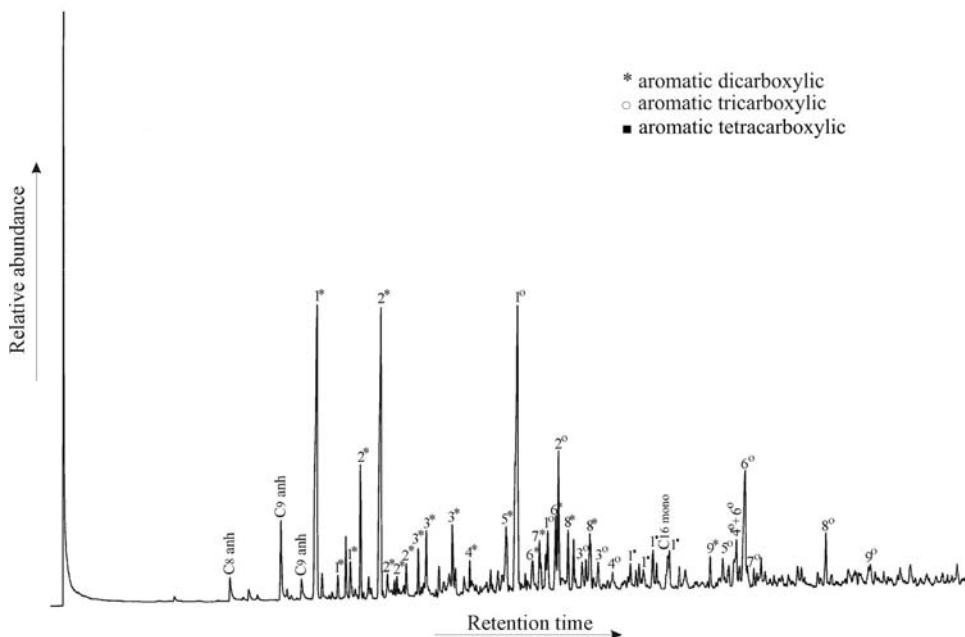


Fig. 3. Gas chromatogram of the ether-soluble acids Ty 4 (1), in the form of methyl esters.  
See Appendix.

The GC–MS analysis of the two fractions of ether-soluble acids (including the acids isolated from the corresponding aqueous solutions) revealed the presence of different saturated normal and branched mono- and dicarboxylic and alkane tri- and tetracarboxylic acids as the major constituents, different aromatic mono-, di-, tri- and tetracarboxylic acids, as well as minor amounts of saturated hydrocarbons and DHA. The acids identified as oxidation products of the precipitated acids are listed in Table II.

TABLE I. Ether-soluble acids and related compounds obtained by oxidation of kerogen (including acids isolated from the corresponding aqueous solutions)

Compound		From kerogen <sup>a</sup> Ty 1-6 (1)	From aqueous solutions <sup>a</sup> Ty 1-6 (2)
Aromatic acids <sup>b</sup>	mono-	C <sub>8</sub> H <sub>9</sub> -; C <sub>12</sub> H <sub>17</sub> -; C <sub>10</sub> H <sub>7</sub> - <sup>b</sup> ; C <sub>11</sub> H <sub>9</sub> - <sup>b</sup> ; C <sub>12</sub> H <sub>11</sub> - <sup>b</sup> ; C <sub>13</sub> H <sub>13</sub> - <sup>b</sup> ; C <sub>16</sub> H <sub>19</sub> - <sup>b</sup> ; C <sub>24</sub> H <sub>35</sub> - <sup>b</sup>	C <sub>11</sub> H <sub>15</sub> -; C <sub>12</sub> H <sub>17</sub> -; C <sub>22</sub> H <sub>37</sub> -; C <sub>11</sub> H <sub>9</sub> - <sup>b</sup> ; C <sub>21</sub> H <sub>29</sub> - <sup>b</sup> ; C <sub>23</sub> H <sub>33</sub> - <sup>b</sup> ; C <sub>24</sub> H <sub>35</sub> - <sup>b</sup>
	di-	C <sub>6</sub> H <sub>4</sub> =; C <sub>7</sub> H <sub>6</sub> =; C <sub>8</sub> H <sub>8</sub> =; C <sub>9</sub> H <sub>10</sub> =; C <sub>10</sub> H <sub>12</sub> =; C <sub>11</sub> H <sub>14</sub> =; C <sub>10</sub> H <sub>6</sub> = <sup>b</sup> ; C <sub>11</sub> H <sub>8</sub> = <sup>b</sup> ; C <sub>12</sub> H <sub>10</sub> = <sup>b</sup> ; C <sub>14</sub> H <sub>14</sub> <sup>b</sup> ; C <sub>16</sub> H <sub>18</sub> = <sup>b</sup>	C <sub>6</sub> H <sub>4</sub> =; C <sub>7</sub> H <sub>6</sub> =; C <sub>8</sub> H <sub>8</sub> =; C <sub>9</sub> H <sub>10</sub> =; C <sub>11</sub> H <sub>14</sub> =; C <sub>11</sub> H <sub>8</sub> = <sup>b</sup> ; C <sub>12</sub> H <sub>10</sub> = <sup>b</sup> ; C <sub>23</sub> H <sub>32</sub> = <sup>b</sup>
	tri-	C <sub>6</sub> H <sub>3</sub> =; C <sub>7</sub> H <sub>5</sub> =; C <sub>8</sub> H <sub>7</sub> =; C <sub>9</sub> H <sub>9</sub> =; C <sub>10</sub> H <sub>11</sub> =; C <sub>11</sub> H <sub>13</sub> =; C <sub>16</sub> H <sub>23</sub> =; C <sub>10</sub> H <sub>5</sub> = <sup>b</sup> ; C <sub>11</sub> H <sub>7</sub> = <sup>b</sup> ; C <sub>14</sub> H <sub>13</sub> = <sup>b</sup> ; C <sub>16</sub> H <sub>17</sub> = <sup>b</sup> ; C <sub>17</sub> H <sub>19</sub> = <sup>b</sup>	C <sub>6</sub> H <sub>3</sub> =; C <sub>7</sub> H <sub>5</sub> =; C <sub>8</sub> H <sub>7</sub> =; C <sub>10</sub> H <sub>11</sub> =; C <sub>16</sub> H <sub>23</sub> =; C <sub>10</sub> H <sub>5</sub> = <sup>b</sup> ; C <sub>11</sub> H <sub>7</sub> = <sup>b</sup> ; C <sub>12</sub> H <sub>9</sub> = <sup>b</sup> ; C <sub>16</sub> H <sub>17</sub> = <sup>b</sup>
	tetra-	=C <sub>6</sub> H <sub>2</sub> =; =C <sub>10</sub> H <sub>10</sub> =; =C <sub>16</sub> H <sub>22</sub> =	=C <sub>6</sub> H <sub>2</sub> =; =C <sub>7</sub> H <sub>4</sub> =; =C <sub>10</sub> H <sub>10</sub> =; C <sub>16</sub> H <sub>22</sub> =
Aliphatic acids	mono-	nC <sub>16</sub> ; nC <sub>18</sub>	nC <sub>16</sub> ; nC <sub>18</sub> ; nC <sub>24</sub> ; C <sub>17</sub> br
	di-	—	nC <sub>5</sub> ; nC <sub>7</sub> ; nC <sub>8</sub> ; C <sub>5</sub> br; C <sub>6</sub> br
Anhydrides		C <sub>8</sub> ; C <sub>9</sub>	C <sub>8</sub> ; C <sub>9</sub>
Saturated hydrocarbons		—	C <sub>21</sub> -C <sub>32</sub>

<sup>a</sup>The individual isomers of the various oxidation products were not identified. Hence, the proposed R groups are tentative. They may represent any other possible combination of R groups. Free valences indicate carboxylic groups; <sup>b</sup>naphthalene-carboxylic acids

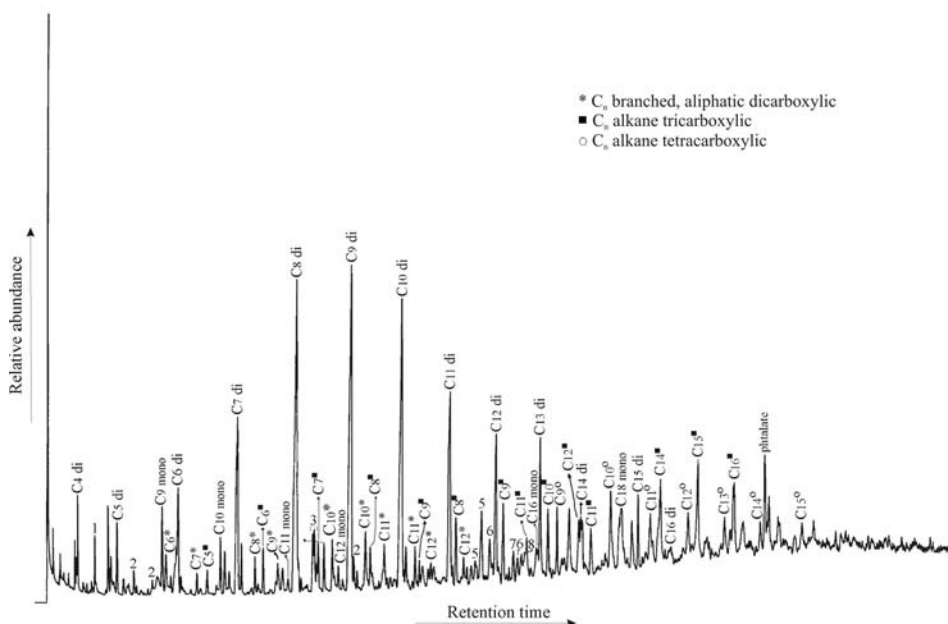


Fig. 4. Gas chromatogram of the ether-soluble acids Ty P 1 (1), in the form of methyl esters. See Appendix.

## DISCUSSION

A detailed structural study of a type III kerogen originating from a Tyrolean (Austria) "Hauptdolomit" Triassic sediment was carried out, aimed at obtaining evidence on the relationship between a type III kerogen and the yields and chemical nature of the degradation products produced using an optimized alkaline permanganate oxidation method. The results served as a basis for the reconstruction of the kerogen structure. They are also expected to be a basis for comparison with the structure of other type III kerogens, in particular with the structure of the type III Mannville shale kerogen, the single type III kerogen hitherto studied under similar experimental conditions.<sup>8</sup>

TABLE II. Ether-soluble acids and related compounds obtained by oxidation of precipitated acids (including acids isolated from the corresponding aqueous solutions)

Compound		From precipitated acids <sup>a</sup> Ty P 1-2 (1+2)
Aromatic acids	mono-	C <sub>6</sub> H <sub>5</sub> -; C <sub>7</sub> H <sub>7</sub> -; C <sub>11</sub> H <sub>9</sub> - <sup>b</sup> ; C <sub>14</sub> H <sub>15</sub> - <sup>b</sup>
	di-	C <sub>6</sub> H <sub>4</sub> =; C <sub>7</sub> H <sub>6</sub> =; C <sub>10</sub> H <sub>12</sub> =; C <sub>10</sub> H <sub>6</sub> = <sup>b</sup> ; C <sub>11</sub> H <sub>8</sub> = <sup>b</sup> ; C <sub>12</sub> H <sub>10</sub> = <sup>b</sup>
	tri-	C <sub>6</sub> H <sub>3</sub> ≡; C <sub>7</sub> H <sub>5</sub> ≡; C <sub>9</sub> H <sub>9</sub> ≡; C <sub>11</sub> H <sub>7</sub> ≡ <sup>b</sup>
	tetra-	=C <sub>6</sub> H <sub>2</sub> =
Aliphatic acids	mono-	nC <sub>9</sub> -C <sub>12</sub> ; nC <sub>14</sub> -C <sub>18</sub> ; nC <sub>22</sub> -C <sub>24</sub> ; nC <sub>26</sub> ; C <sub>17</sub> br; C <sub>19</sub> br
	di-	nC <sub>4</sub> -C <sub>17</sub> ; C <sub>5</sub> -C <sub>12</sub> br
Alkane-poly-carboxylic acids	tri-	C <sub>3</sub> -C <sub>12</sub> ; C <sub>14</sub> -C <sub>19</sub>
	tetra-	C <sub>5</sub> -C <sub>15</sub>
Saturated hydrocarbons		C <sub>21</sub> -C <sub>24</sub> ; C <sub>26</sub> -C <sub>29</sub>
Diterpenoids		DHA

<sup>a</sup>The individual isomers of the various oxidation products were not identified. Hence, the proposed R groups are tentative. They may represent any other possible combination of R groups. Free valences indicate carboxylic groups; <sup>b</sup>naphthalene-carboxylic acids

The twenty-nine step alkaline permanganate degradation of Tyrolean shale kerogen resulted in a very high total yield of oxidation products, 93.7 % based on the original kerogen, comprising neutrals and bases (0.5 %), ether-soluble acids (11.0 %), acids isolated from the corresponding aqueous solutions (8.5 %), precipitated acids (58.9 %), and 14.8 % of kerogen carbon in the form of carbon dioxide, an oxidation product quantified by a modified method of Partridge and Schroeder.<sup>12,13</sup> The amount of residual organic matter remaining after the last oxidation step was 6.9 %, making the total material balance 100.6 %, which included the permanganate oxygen incorporated into the oxidation products.

The observed high yields of the recovered oxidation products suggested that the material losses during the complex experimental procedure were rather low. However, material losses cannot be completely excluded.

The solubility of the oxidation products in diethyl ether was found to be relatively low, the ratio of precipitated (ether-insoluble) vs. ether-soluble acids (PA/ESA) being quite high, 3.02.



The qualitative and quantitative compositions of the oxidation products obtained by degradation of Tyrolean shale kerogen are shown in Tables I and III.

The composition of the ether-soluble acids was surprising: 0.8 % C<sub>16</sub> and C<sub>18</sub> alkane-monocarboxylic acids, no alkane-dicarboxylic acids, and practically 99 % aromatic acids (Tables I and II), with almost 60 % of the dominating aromatic dicarboxylic acids. The acids isolated from the concentrated aqueous solutions had a somewhat different composition: *ca.* 1.2 % of alkane-mono- and dicarboxylic acids of narrow range and simple distribution, the rest representing aromatic acids, the composition of which differed from the corresponding composition of the ether-soluble aromatic acids, due to the higher solubility of polycarboxylic aromatic acids (Tables I and II).

TABLE III. Composition of oxidation products obtained by degradation of Tyrolean oil shale kerogen

Acids	Content relative to identified acids, %						Total I + II
	Oxidation of kerogen			Oxidation of precipitated acids			
	Ether soluble acids	Acids from aqueous solutions	Total I	Ether soluble acids	Acids from aqueous solutions	Total II	
Alkane carboxylic acids							40.7
<i>n</i> -Mono-acids	0.83	0.41	0.66	4.28	9.24	4.69	3.2
<i>n</i> -Br-mono-	—	—	—	—	1.63	0.13	0.1
<i>n</i> -Di-	—	0.63	0.22	52.14	37.76	50.95	32.8
br-Di-acids	—	0.17	0.06	7.68	1.75	7.19	4.6
Alkane polycarboxylic acids							16.3
Tricarboxylic	—	—	—	16.32	15.06	16.22	10.4
Tetracarboxylic	—	—	—	9.20	9.79	9.25	5.9
Aromatic acids							43.0
Monocarboxylic	2.53	6.24	3.77	3.15	3.16	3.15	3.3
Dicarboxylic	59.19	24.05	47.82	4.61	11.73	5.20	20.0
Tricarboxylic	32.31	42.16	35.04	2.32	8.60	2.84	14.0
Tetracarboxylic	5.15	26.34	12.43	0.30	1.27	0.38	4.6
Anhydride of al- kyl phthalic acid				—			1.1

Histograms illustrating the ranges and distributions of the total alkane-mono- and dicarboxylic acids observed after kerogen degradation are shown in Figs. 5a and 6a.

Alkane-mono-carboxylic acids were isolated in very low yields. They were composed exclusively of C<sub>16</sub> and C<sub>18</sub> members. Hence, they were most probably linked to the kerogen matrix by ester-type bonds.

The major aromatic components in the ether-soluble acids, including those isolated from the corresponding aqueous solutions, were different substituted benzene- and naphthalene-mono-, di- and tricarboxylic acids, as well as benzene-

-tetracarboxylic acids (Table I). Low amounts of phthalic acid anhydride and saturated hydrocarbons (contamination) were also identified. The most abundant were benzene-dicarboxylic acids (from  $C_6H_4=$  up to  $H_{11}C_5\cdot C_6H_3=$ ), naphthalene-dicarboxylic acids (from  $C_{10}H_6=$  up to  $H_{27}C_{13}\cdot C_{10}H_5=$ ), benzene-tricarboxylic acids (from  $C_6H_3\equiv$  up to  $H_{21}C_{10}\cdot C_6H_2\equiv$ ) and naphthalene-tricarboxylic acids (from  $C_{10}H_5\equiv$  up to  $H_{15}C_7\cdot C_{10}H_4\equiv$ ).

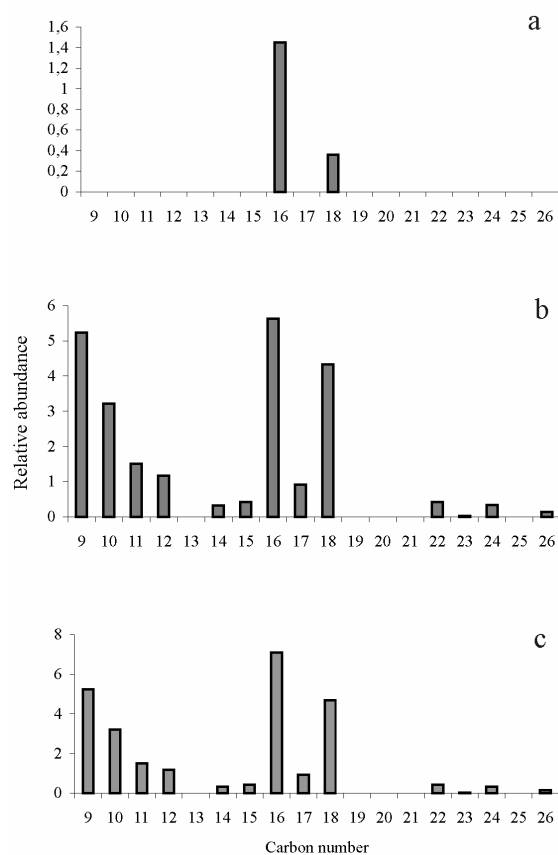


Fig. 5. Relative abundance and distribution of *n*-monocarboxylic acids obtained by oxidative degradation of kerogen (a) and precipitated acids (b), and their total abundance and distribution (c).

Reconstruction of the original macromolecular structure of the Tyrolean shale kerogen based exclusively on the composition of its ether-soluble acidic oxidation products obtained in a moderate yield, *i.e.*, 19.5 % relative to kerogen, can only be tentative. Nevertheless, taking into consideration, in addition to the composition of ether-soluble acids, the amount of kerogen carbon oxidized into  $CO_2$  (14.8 %), the degradation products of at least one part of the kerogen suggest cross-linking and substitution in its structure by very short alkyl chains as well as slight aryl-substitution, resulting in a low yield of aromatic monocarboxylic acids. The proportion of aromatic tetracarboxylic acids indicates a limited amount of condensed aromatic structural elements in this part of the kerogen. On the other

hand, the high proportions of aromatic tricarboxylic and particularly dicarboxylic acids indicate precursor aromatic structures cross-linked by short *n*- or eventually branched aliphatic or alicyclic hetero-functional chains, and characterized by methyl-substitution.

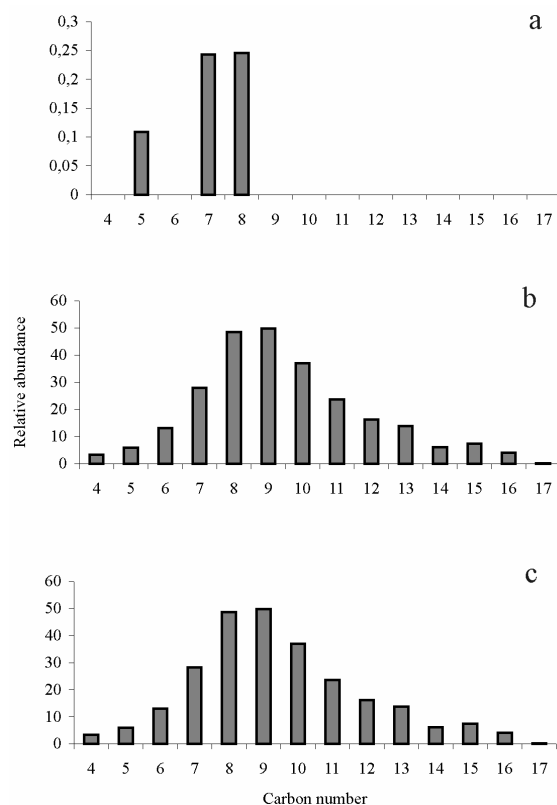


Fig. 6. Relative abundance and distribution of  $\alpha,\omega$ -dicarboxylic acids obtained by oxidative degradation of kerogen (a) and precipitated acids (b), and their total abundance and distribution (c).

Heterocyclic structures probably are not constituents of this part of kerogen, since alkane-polycarboxylic acids were not observed in the oxidation products. On the other hand, the degradation residue, being relatively high, 6.9 %, suggests that Tyrolean shale kerogen contains structures resistant towards alkaline permanganate.

The degradation of kerogen and the observed PA/ESA ratio indicates structural non-homogeneity of the kerogen matrix, *i.e.*, the existence of at least two structural entities, one abundant in cross-links sensitive to oxidative cleavage and the other consisting of bulky units with cross-links less sensitive towards oxidative degradation.

However, as mentioned, the final structural interpretation of the kerogen depended on the investigation of the degradation products of the precipitated, ether-insoluble acids, which were the main kerogen degradation product.

Qualitative and quantitative data observed in the further degradation of the precipitated acids gave a completely different image of the kerogen structure (Tables II and III). Ether-soluble acids were obtained in *ca.* 59.0 % yield relative to the precipitated acids. On the other hand, 29.3 % of the total precipitated acids (17.3 % relative to kerogen) remained after the eighth oxidation step in the form of a non-degraded residue, *i.e.*, they were resistant towards the oxidant.

The ratio of aliphatic *vs.* aromatic acids differed substantially from the corresponding ratio observed in the degradation of the kerogen (Table III). Surprisingly, aliphatic *n*-mono- and particularly *n*- and branched  $\alpha,\omega$ -dicarboxylic, as well as alkane-tri- and tetracarboxylic acids were the major oxidation products of the precipitated acids (63.0 %). Aromatic mono- to tetracarboxylic acids represented minor oxidation products, 11.6 %. Long-chain acids dominated among the aliphatic acids, 50.9 % of these being C<sub>4</sub>–C<sub>17</sub> *n*-alkane-dicarboxylic acids, with a maximum at C<sub>9</sub> (a histogram is shown in Fig. 6b) and 7.2 % were branched alkane-dicarboxylic acids. Monocarboxylic acids were obtained in lower yield. Their range (C<sub>9</sub>–C<sub>26</sub>) and distribution is illustrated by the histogram shown in Fig. 5b. The alkane-di-/alkane-monocarboxylic acids ratio was high, 10.9. The observed data give a different picture of the proportion and type of alkyl-substituents and the proportion, structure and length of the aliphatic cross-links in the precipitated acids from Tyrolean shale kerogen. The degradation loss was 10.6 % relative to the initial precipitated acids.

The ranges of the aromatic di- and tricarboxylic acids were simpler compared to the aromatic acids identified in the ether-soluble oxidation products of the kerogen (Tables II and III).

Hence, the data obtained from the further degradation of the precipitated acids corroborated the presumption concerning the heterogeneity of the Tyrolean shale kerogen.

Finally, the amount of residual precipitated acids resistant towards further stepwise oxidative degradation, as mentioned, was rather high, 17.3 % relative to kerogen. Consequently, in total, approximately 24 % of the kerogen (6.9 % in kerogen degradation plus 17.3 % in degradation of the precipitated acids) was found to be resistant towards alkaline permanganate. On the other hand, the material loss (CO<sub>2</sub> plus low molecular weight acids remaining in the aqueous solutions) during the further degradation of the precipitated acids was 6.3 %. Together with the 14.8 % loss (quantified as CO<sub>2</sub>) observed in the degradation of kerogen, the total loss was 21 %, originating mainly from C<sub>1</sub>–C<sub>3</sub> alkyl substituents and/or short aliphatic chain cross-links.

Since the yields of aliphatic, alkane-polycarboxylic and aromatic acids, as the main oxidation products of the aliphatic, alicyclic and/or heterocyclic and aromatic components of the kerogen matrix, were proposed as a basis for the classification of kerogens,<sup>9</sup> the corresponding values observed in the degradation of

the Tyrolean shale kerogen (Table III) were introduced into a triangular diagram shown in Fig. 7. The diagram includes corresponding positions of several other kerogens hitherto examined by the same degradation method.

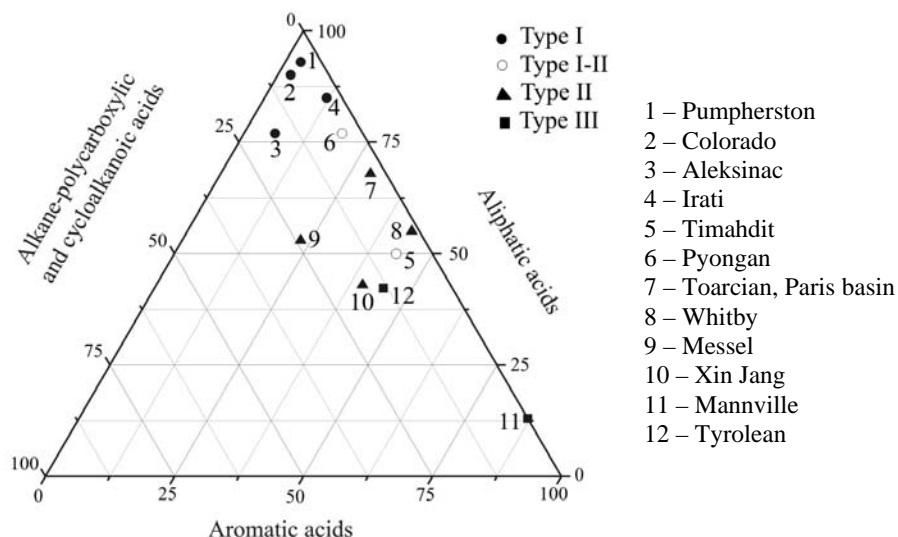


Fig. 7. Composition of the oxidation products obtained by degradation of Tyrolean shale kerogen and of several other kerogens.

Combining the yields of the oxidation products of Tyrolean shale kerogen and precipitated acids, both calculated relative to the original kerogen, one comes to a balance between the aromatic, alkane mono- and dicarboxylic and alkane-polycarboxylic acidic oxidation products which suggests a shift of the structure of Tyrolean shale kerogen from the expected typical aromatic type III kerogen towards a heterogeneous aromatic-aliphatic-alicyclic type structure, *i.e.*, towards some kind of intermediate type III-II kerogen.

The estimated structure of the Tyrolean shale kerogen based on oxidative degradation products shown in the triangular diagram (Fig. 7) obviously differs substantially from the estimated structure of type III Mannville shale kerogen, based also on multistage alkaline permanganate degradation. This difference, however, may be explained by the fact that methods used for the oxidative degradation of these two type III kerogens were different. Namely, the Mannville shale kerogen was studied<sup>8</sup> before the alkaline permanganate degradation method had been optimized by the addition of the isolation and identification of acids from aqueous solutions and the determination of the amount of kerogen carbon oxidized into carbon dioxide.<sup>13</sup> Thus, in the degradation procedure of Mannville shale kerogen at that time, a part of its structure, yielding acids highly soluble in water, and methyl or short aliphatic chain substituents and cross-links, yielding CO<sub>2</sub> on oxidation with alkaline permanganate, were neglected. Therefore, the estimation of the

structure of Mannville shale kerogen based on alkaline permanganate oxidative degradation must be reappraised before comparison of its structure with the estimated structure of Tyrolean shale kerogen.

Likewise, neither the so-called kerogen nor the precipitated acid residues resistant to degradation should be neglected, particularly when their proportion is shown to be as high as in the degradation of Tyrolean shale kerogen. Namely, the H/C ratio of the latter (0.76) indicated an overall aromaticity which, however, was not confirmed through the yield of aromatic acids obtained as its oxidation products. Consequently, the Tyrolean shale kerogen and precipitated acids residues, observed in a total yield of 24 % relative to kerogen, are suggested to be in the form of resorcinol units linked by ether bonds. Such a presumption is based on chemical and geochemical evidence. On the one hand, resorcinol structures are known to be resistant towards alkaline permanganate. On the other hand, continental (terrestrial) flora residues consisting of lignin (generally resorcinol) structures, diagenetically resistant dominant biostructures, are often type III precursors.

#### CONCLUSIONS

Experimental data observed by stepwise oxidative degradation of Tyrolean oil shale type III kerogen, and further degradation of the resulting insoluble (precipitated) acids, as well as the results of detailed qualitative and quantitative analyses of the obtained acidic oxidation products suggest the following conclusions.

Tyrolean oil shale kerogen is a heterogeneous macromolecular substance consisting of three types of structures, differing in composition and susceptibility towards alkaline permanganate as an oxidant.

One type is composed of quite resistant structures, presumably consisting of aromatic units cross-linked by resorcinol ethereal bonds, its estimated proportion in the kerogen matrix being *ca.* 24 %.

The second type of structure is, on the one hand, aliphatic in nature, comprising abundant methyl-substituents and shorter chain cross-links, both easily oxidized into "non-isolated" products such as CO<sub>2</sub>, water, and low molecular weight acids. Their proportion in the kerogen matrix is estimated to be *ca.* 21 %. These cross-links consolidate the aromatic components which, upon oxidation, are converted into high yields of aromatic di- and tricarboxylic acids.

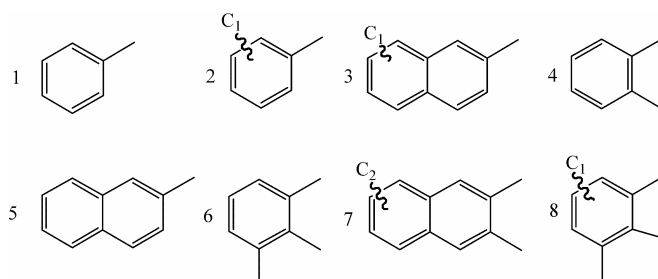
The third type, moderately resistant towards oxidation, is composed of aliphatic-alicyclic (and/or heterocyclic) structures, mutually bound into units containing low proportion of aromatic structures.

Although classified as type III kerogen and characterized by a significantly high vitrinite reflectance ( $R_o = 1.38$ ), its oxidative degradation produced a high total yield of alkane-mono- and dicarboxylic acids. They were of unusually simple ranges, particularly the identified *n*-alkane-monocarboxylic acids, and simple distributions, which were also uncommon, indicating the existence of precursor aliphatic structural elements of relatively homogenous composition and structure.

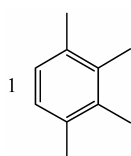
The rather high proportion of acidic oxidation products (4.6 %) consisting for the most part of branched alkane-dicarboxylic acids, with just a small proportion of branched alkane-monocarboxylic acids, obviously originated from the corresponding branched structural elements in the kerogen matrix. Such a high proportion of these structures in kerogen oxidation products seems to be a specificity of type III kerogens inherited from a terrestrial precursor biomass.

A high yield of alkane-polycarboxylic (tri- and tetracarboxylic) acids (16.3 %) originates from a similar high proportion of precursor alicyclic/heterocyclic structures in the kerogen matrix, which probably also may be considered as unexpected for a type III kerogen.

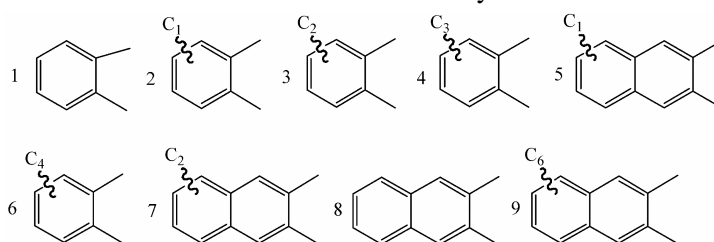
## APPENDIX

*Appendix to Fig. 3**Appendix to Fig. 4*

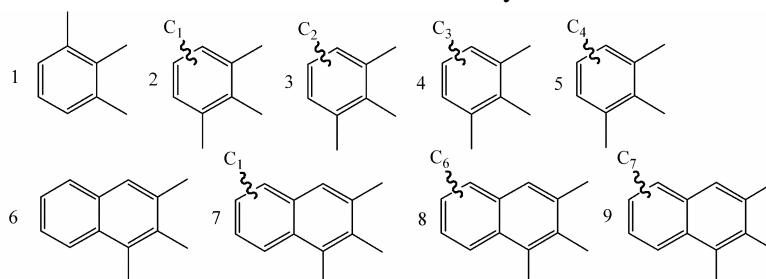
■ – Aromatic tetracarboxylic



\* – Aromatic dicarboxylic



○ – Aromatic tricarboxylic



## ИЗВОД

## КАРАКТЕРИЗАЦИЈА КЕРОГЕНА ТИПА III ТИРОЛСКОГ ШКРИЉЦА (НАНТЕННЈОШ, АУСТРИЈА) ЗАСНОВАНА НА ЊЕГОВИМ ОКСИДАЦИОНИМ ПРОИЗВОДИМА

С. БАЈЦ<sup>1</sup>, О. ЦВЕТКОВИЋ<sup>1</sup>, А. AMBLÈS<sup>2</sup> и Д. ВИТОРОВИЋ<sup>1</sup><sup>1</sup>Центар за хемију, ИХТМ, Њеђошева 12, 11000 Београд и <sup>2</sup>Department of Chemistry, Faculty of Science, University of Poitiers, 40, Av. du Recteur Pineau, 86022 Poitiers, France

Ступњевитом деградацијом керогена тиролског шкриљца помоћу алкалног перманганата добијени су високи приноси оксидационих производа. Добијене нерастворне киселине накнадно су деградоване у 8 ступњева. Детаљна GC-MS анализа киселина растворних у етру, добијених деградацијом керогена, потом интермедијарних нерастворних киселина, показала је да је кероген тиролског шкриљца хетерогена макромолекуларна супстанца и да се састоји из три типа структуре, различитог састава и различите осетљивости на примењено оксидационо средство. Први тип је ароматичне природе са резорцинолним етарским умрежењем, отпоран према алкалном перманганату. Други се врло лако оксидује, а састоји се од ароматичних структура умрежених кратким алифатичним низовима и са већим уделом метил-супституената. Овај тип структуре је при оксидацији дао висок принос CO<sub>2</sub>, алифатичне киселине малих молекулских маса и ароматичне ди- и трикарбоксилне киселине у високом приносу. Трећи тип структуре је средње осетљивости на перманганат, а састоји се од алицикличких и/или хетероцикличких и ароматичних језгара повезаних алифатичним низовима средњих дужина. Квантитативан однос алифатичних, ароматичних и алкан-поликарбоксилних киселина у оксидационим производима показао је да структура керогена тиролског шкриљца одступа од типских, доминантно ароматичних структура типа III, којима припада по свом H/C–O/C атомском односу, и да је померена ка хетерогеним, ароматично-алифатично-алицикличким структурама типа II.

(Примљено 15. октобра, ревидирано 19. новембра 2007)

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